Raman spectral analysis of an organometallic composite film synthesized by electrochemical route

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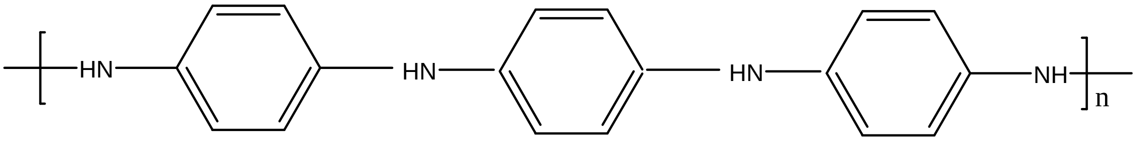
Abstract. The fabrication and characterization of Au-polyaniline (Au-PANI) composite films using electrochemical synthesis are presented. The PANI film is prepared by the chronopotentiometery technique on a Pt substrate. The as deposited PANI film was modified with Au nanoparticles using cyclic voltammetery. X-ray diffraction (XRD), Raman spectroscopy and Scanning electron microscopy (SEM) techniques were used to establish the structural-morphological properties of the Au–PANI composite. XRD spectra revealed (100) and (200) planes in the composite. A SEM image of PANI shows a rough and porous morphology, whereas Au-PANI composite exhibit a mesh type structure with uniform dispersion of the Au nanoparticles. It is observed that the Au-PANI composite showed enhanced Raman characteristics (due to the Surface Enhanced Raman Spectroscopy effect of the Au nanoparticles) in comparison to the pure PANI film. The analysis revealed that the Au-PANI composite can be used for highly sensitive and selective chemical and biological sensing applications.

1. Introduction

Polynailine (PANI) is a conjugated polymer whose chain contains two types of nitrogen atoms: amine (–NH–) and imine (=N–). The chemical structure of PANI may be presented as follows:



The ratio of imino nitrogen to amino nitrogen determines the conductive state of PANI. Nitrogen atoms present in the structure of PANI offers potential sites for PANI-metal complexes interaction and are responsible for the strong affinity towards the metal ions for modifying the functional properties in the organometallic composites.

Organometallic composites offer a great opportunity to be exploited in sensing devices, catalysis materials, super capacitors, batteries, EMI, solar cells, etc. [1-3] The insertion of metal particles on the surface of polymers projects new ways and means to enhance the electrochemical, optical and electro catalytic performance thereof. It also broadens their applications in other diverse domains [4-6]. Various synthetic methods such as chemical, electrochemical, sol-gel, self-assembly and radiolysis are adopted for the fabrication of organometallic composites [7-8]. In order to improve the functional properties of the Au-PANI composite a facile technique is reported by modifying the surface of the PANI films by Au-metal particles in an acidic solution. Recent studies confirm that metal conducting polymer composites are useful substrates for SERS (Surface Enhanced Raman Spectroscopy) [9-10]. These substrates are highly sensitive and cost effective.

In this study the electrochemical route is applied for the synthesis of rough surface PANI films. The surface is modified by Au particles to enhance its surface sensitivity.. In this synthesis process the nitrogen atoms are used as sites for a selective doping process and are responsible for the strong affinity with the Au^{2+} cations for modifying the functional properties in the composites. This work is related to the surface modification of PANI films by making the co-ordination between imine sties of PANI with the Au^{2+} cations. Chronopotentiometery is used for the fabrication of PANI films and later the synthesized surface of the films is modified by the Au-particles using cyclic voltammetry (CV) which shows strong redox reactivity occurring during synthesis. It should be noted that the system selected for the present studies are of practical importance due to their potential to improve the functional properties in chemical and biochemical sensing. This study shows the systematic interaction between metal and organic compounds.

2. Experimental

2.1. Material

Aniline monomer (Merck, 99.5% purity), pTS (Merck, 99%) and HNO_3 were used as starting materials in the present study. All the reagents were of analytical grade and used without further purifications. All the experiments were carried out with double-distilled water.

Electrochemical synthesis was carried out using a CHI 660D electrochemical workstation. The standard three electrode setup was employed in a one compartment electrochemical cell. A rectangular conducting indium tin oxide (ITO) sheet of size $20 \times 10 \times 0.7$ mm^3 was used as a working electrode whereas a Pl sheet of size $20 \times 40 \times 0.25$ mm^3 was used as a counter electrode. The reference electrode was an Ag/AgCl electrode. The first step involves the aqueous electro polymerization of aniline containing a 80 ml aqueous solution onto an ITO substrate using a chronopotentiometery technique. The electrolyte solution was composed of 0.15 M aniline monomer and 0.60 M pTS. The surface modification of the synthesized PANI film was conducted in an aqueous solution of 80 ml containing 0.0002 M $HAuCl_4$ and 0.005 M HNO_3 using CV between potential windows of 0.0 to 1.0 V at a scan rate of 30 mV s^{-1}. The surface of the PANI film was uniformly decorated with Au nanoparticles by controlling the scan rate and applied potential during the synthesis process. The thickness of the synthesized composite film was 20 ± 2 µm.

Scanning electron microscopy (SEM) images were obtained using a JSM-6490LV Joel at 25 keV after covered with a thin layer (~15 nm) of sputtered gold. The micro-RAMAN investigation was carried out using a Renishaw InVia Raman micro-scope. The Ar ion laser excitation at 514 nm at a very low power (<1 mW, 20× objective) was used to avoid any heating effects. X-ray diffraction (XRD) patterns of the Au-PANI composite film was recorded on a Phillips X-ray diffractometer with

Cu-Kα radiation (1.54˚A) for a wide range of Bragg's angle 2θ ($20^0 < \theta < 50^0$) at a scanning rate of 1^0 per min. The operating voltage and current for the X-ray gun were 40 kV and 40 mA, respectively.

3. Results and discussion

The electrochemical synthesis of PANI on ITO substrates using chronopotentiometery was investigated as a function of various reaction parameters that seem to influence the formation of the PANI films (Fig. 1). A porous film with a rough surface was obtained at a low polymerization potential during the first step of the electrochemical synthesis (see SEM images in the next section). The prepared film was immersed in an acidic solution of 0.005 M HNO_3 containing 0.0002 M $HAuCl_4$ for the surface modification of the PANI film using CV (Fig. 1). The scan rate was kept at 30 mV/s for less sweep segments in a potential range 0.0 V to 1 V during CV. The redox process is initiated with the dissociation of $HAuCl_4$ into cations and anions followed by further oxidation of the NO_3^- at the anode. The formation of Au ions and the subsequent reduction at the working electrode is well established as shown in Fig. 2. The cathodic peak indicates the reduction of Au-particles on the surface of the PANI film and the oxidation peak clearly represents the formation of imine nitrogen for reducing more Au-particles.

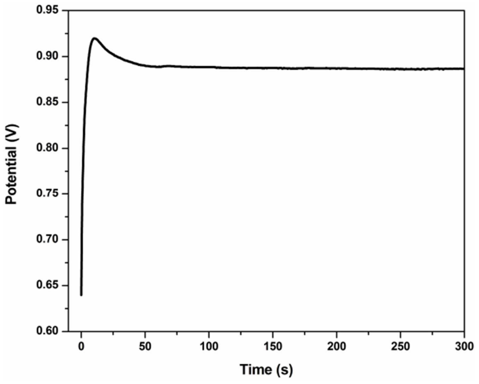


Fig. 1 Chronopotentiogram recorded during the synthesis of the PANI film.

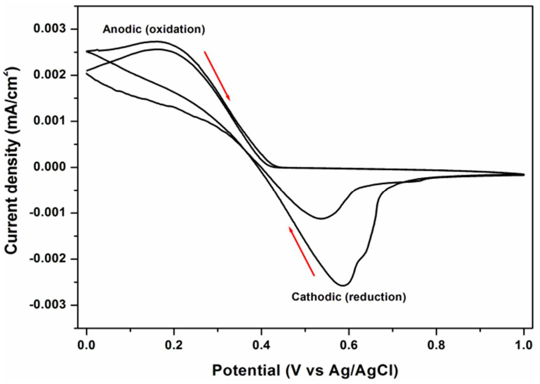


Fig. 2 The CV of the Au-PANI film between potential windows of 0.0 V to 1.0 V in a solution of $HAuCl_4$+HNO_3 in a ratio 0.0002:0.005, respectively with scan rate of 30 mV s^{-1}.

3.1. SEM results

SEM is carried out to provide confirmation of the PANI film and decoration of the film with Au nanoparticles on the surface of the PANI film. Fig. 3(a)-(b) shows the SEM images of the PANI and the Au-PANI composite films.

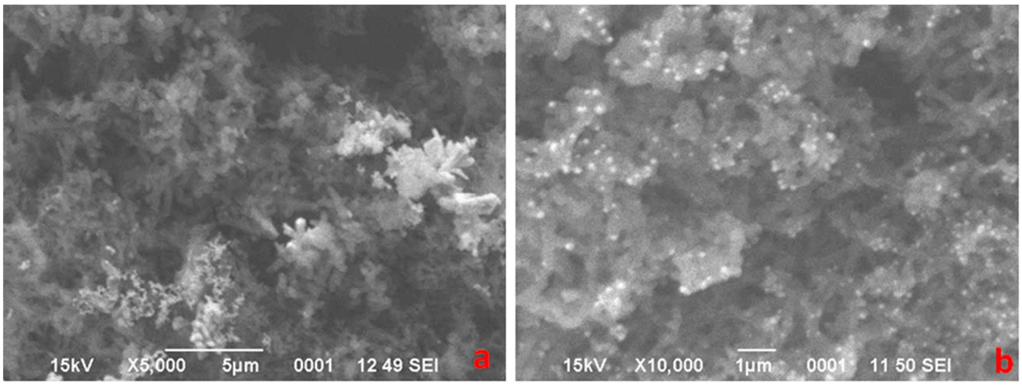


Fig. 3 SEM images of (a) PANI and (b) Au-PANI composite film

From Fig. 3(a), it is clear that the PANI film shows micro rods with a rough surface morphology. Moreover, the PANI film shows a fibrous network with porous structures.

Fig. 3(b) shows that Au particles were uniformly dispersed on the PANI surface indicate the coupling of the Au particles with the surface of the PANI film. The Au particles appear as white spots on the PANI film. Moreover, the image shows homogeneous distribution of the Au particles on the rough surface of the PANI film, which indicates their reliability in using as a SERS substrate [11-13].

3.2. X-ray diffraction analysis

The structural characteristics of the Au-PANI composite have been analysed by XRD and are shown in Fig. 4. The peaks between 2θ = 21.36°, 25.12 and 27.26° is the characteristic peaks of PANI [14]. The prominent peaks corresponding to 2θ = 38.12° and 44.28° are due to (111) and (200) planes of Au and indicate the presence of Au particles in the Au-PANI composite. Furthermore, it confirmed the Au particles retained its structure. Hence it is reasonable to accept that Au in the Au-PANI composite is accountable for the SERS and other properties.

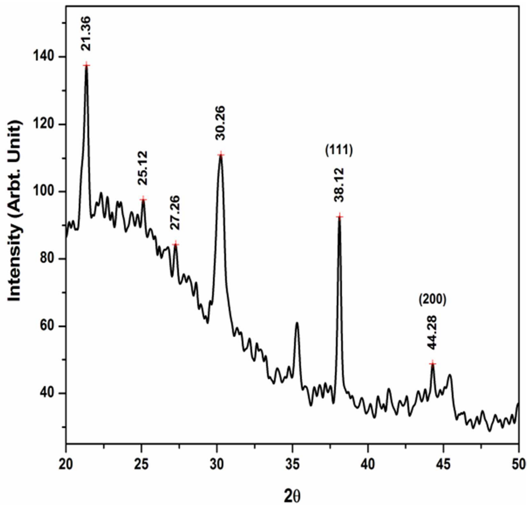


Fig. 4 XRD pattern of the Au-PANI composite film.

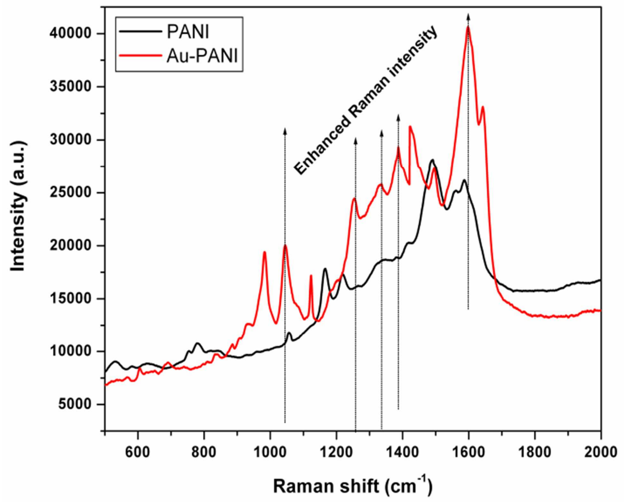


Fig. 5 Raman spectra of the PANI and Au-PANI composite films.

3.3. Raman studies of the Au-polyaniline composite film

The Raman spectra of PANI and Au-PANI composite films are shown in Fig. 5. The bands in the wavenumber range of 1100 to 1700 cm^{-1} corresponds to the stretching modes of different bonds. The benzene C–H bending deformation mode lies at 1140 to 1190 cm^{-1} for the reduced semiquinone and quinoid ring structure. The different C–N stretching mode (amines, imines, and polarons) lies between 1210 and 1520 cm^{-1}. The Raman band at 1586 cm^{-1} is attributed to the C–C stretching vibration of a benzene ring [15]. The band at 1254 cm^{-1} can be assigned to the C–N stretching mode of the polaronic units. The band at 1336 cm^{-1} corresponds to the C–N$^{\bullet+}$ stretching modes of the delocalized polaronic charge carriers [16]. A low intensity band at 1495 cm^{-1} corresponds to the bending deformation of the N$^{\bullet+}$–H unit. The bands at 1320, 1340, 1478 and 1495 cm^{-1} are assigned to C-N, protonated C-N+, C=N and protonated C=N^{+} according to literature [17]. The band at 1165 cm^{-1} represents the C-H bending vibration in the aromatic ring [18]. The observed Raman bands for PANI film are in good agreement with the literature [19].

It is interesting to compare the spectra of PANI with the Au-PANI composite. The Raman shifts and relative intensity observed in the PANI and Au-PANI spectra are listed in Table 1. The Raman spectrum of Au-PANI shows a doublet with bands at 1387 and 1421 cm^{-1} coupled with the C–N$^{\bullet+}$

polarons [20]. This doublet is consistent with the Raman spectrum of metallic PANI [21]. Here, remarkable increases in the intensity of the Au-PANI composite bands were observed with respect to pure PANI bands (Table 1). This remarkable increase in the Raman intensity may be due to the SERS effect of Au-particles on the surface of PANI. This shows the strong interaction of Au ions with the imines sites of PANI after the reduction of Au ions on the nitrogen atom hence alteration of quinoid units into benzoid in the PANI backbone [22].

Baibarac et al. [11-13] investigated the SERS spectra of PANI thin films on rough Au, Ag and Cu substrates. They further suggested that SERS spectra of PANI depend on the oxidizing properties of the metallic surface which reflect that chemical reactions take place at the PANI/metal interface. Barnard and Goff [23] reported a significant enhancement in the band at 1350 cm^{-1} for PANI with Au particles. According to them this band is related to vibrations due to C-N segments. Saheb and Seo [22] reported that the enhancement at 1350 cm^{-1} is more significant when the PANI was electro polymerized in the presence of gold nanoparticles. This clearly shows the enhanced Raman scattering in Au-PANI composites. This suggests that surface decoration of PANI films with Au particles enhances the Raman intensity.

Table 1 Band position and Raman intensity for PANI and Au-PANI composite

Polyaniline		**Au-polyaniline**	
Band position (cm^{-1})	Intensity (a.u.)	Band position (cm^{-1})	Intensity (a.u.)
1586	26178	1597	40629
1491	28137	1495	27329
1218	17304	1421	31271
1165	17826	1387	29324
1056	11790	1254	24448
778	10763	1123	17196
531	9044	1044	20055
		983	19412
		690	8948
		604	8413

4. Conclusion

Au-PANI composite films have been synthesized successfully with a two steps electrochemical technique. XRD patterns confirmed the presence of Au particles in the composite. Interestingly, the Raman spectrum of the Au-PANI composite shows significant enhancement in the Raman intensity. SEM image shows porous and rough surface morphology of the PANI film reflecting better substrates for SERS activity. This enhancement in the Raman intensity in the Au-PANI composite film indicates their possible use in the chemical and biochemical sensing applications.

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